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(54) HOT DIP GALVANNEALED STEEL SHEET EXCELLENT IN FORMABILITY AND ITS PRODUCTION

(57)Abstract:

PROBLEM TO BE SOLVED: To produce a hot dip galvannealed steel sheet excellent in formability and efficiently producible at a low cost and to provide a method for producing it.

SOLUTION: The hot dip galvannealed steel sheet has a surface coating film contg. zinc oxide in which the content of Zn is 100 to 1,000 mg/m2 and one or ≥ two kinds selected from among Fe, Co and Ni of 10 to 1,000 mg/m2 in total on a hot dip galvannealed layer contg., by weight, 7 to 15% Fe, and on whose surface the average crystal grain size is ≤5 μm surface. The steel sheet can be produced by applying the plating on steel by using a hot dip galvanizing bath in which the effective Al concn. is 0.080 to 0.20%, controlling the plating coating weight, thereafter heating it at a temp. of 490 to 550°C at a heating rate of 20 to 70°C/sec, executing alloying treatment and providing the surface with a surface film contg. one or more kinds selected from among Fe, Co and Ni and zinc oxide.

[0015]

[0019]

[0033]

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ABSTRACT:

PROBLEM TO BE SOLVED: To produce a hot dip galvannealed steel sheet excellent in formability and efficiently producible at a low cost and to provide a method for producing it.

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* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]
[Claim 1] the alloying hot-dip-zincing layer top whose surface diameter of average crystal grain Fe is contained seven to 15% of the weight, and is 5 micrometers or less -- the amount of Zn -- 100 - 1000 mg/m2 it is -- a zinc oxide, one sort in Fe, Co, and nickel, or two sorts or more -- the sum total -- 10 - 1000 mg/m2 Alloying hot-dip zinc-coated carbon steel sheet excellent in the moldability characterized by having the surface coat to contain.
[Claim 2] It galvanizes using the melting zinc plating bath whose effective aluminum concentration is 0.080 - 0.20 % of the weight to a base material steel plate. After adjusting plating coating weight, heating at 490 degrees C - 550 degrees C and carrying out alloying processing with the heating rate of 20-70 degrees C/second, maintenance in anodic oxidation and/or oxidizing atmosphere gas -- the amount of Zn -- 100 - 1000 mg/m2 it is -- with the processing to which a plating layer front face is made to be equipped with a zinc oxide The solution containing one sort or two sorts or more of metal ions of Fe, Co, and the nickel is used, and it is this metallic element in total 10 - 1000 mg/m2 The manufacture approach of an alloying hot-dip zinc-coated carbon steel sheet excellent in the moldability according to claim 1 characterized by performing processing made to adhere.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the good alloying hot-dip zinc-coated carbon steel sheet and its manufacture approach of plating-proof detachability at the suitable time of processing for the application to which press working of sheet metal, such as an automobile Body Manufacturing Division article, is performed.
[0002]
[Description of the Prior Art] Although the hot-dip zinc-coated carbon steel sheet is used in large quantities in household electric appliances, building materials, and the industrial field of an automobile in recent years, the alloying hot-dip zinc-coated carbon steel sheet in which economical efficiency, a rust-proofing function, and the engine performance after paint are especially excellent is used widely. An alloying hot-dip zinc-coated carbon steel sheet heats a hot-dip zinc-coated carbon steel sheet to alloying processing temperature, carries out the Fe-Zn alloying of the Zn plating layer, and is manufactured. Plating layer Consisting of a Fe-Zn intermetallic compound, Fe content of the average is usually 8 - 12 % of the weight.
[0003] It is supposed that it is inferior of the press-forming nature (it is only hereafter described also as a "moldability") of an alloying hot-dip zinc-coated carbon steel sheet as compared with the steel plate which does not have a plating layer. It is considered as the cause that, as for it, a surface plating layer bars deformation of the steel plate at the time of shaping. Moreover, that the sliding nature on the front face of plating will worsen, and the inflow resistance to the dice hole of a steel plate will increase at the time of press working of sheet metal if powdering (defect phenomenon in which a plating layer exfoliates in the shape of powder), and a flaking (defect phenomenon in which a plating layer becomes a thin film integrated circuit, and exfoliates on the occasion of press working of sheet metal) occur also becomes the cause that a moldability is spoiled.
[0004] By preparing two or more Fe system alloy electroplating layers on a zinc system plating steel plate, especially an alloying hot-dip zinc-coated carbon steel sheet, and changing surface physical properties to JP,4-202786,A and JP,4-202787,A, the crack initiation of the plating layer which is easy to produce at the time of shaping is prevented, and the technique of raising electropainting nature and a moldability is indicated. However, with the technique currently indicated here, since it was necessary to prepare a multilayer electroplating layer on a hot-dipping layer, the manufacturing cost became high and there was a problem that productivity was also checked.
[0005] The zinc system plating steel plate excellent in the press-forming nature which has the oxide film of a Fe-nickel-O system on a front face on a plating layer, weldability, an adhesive property, and chemical conversion nature is indicated by JP,8-158066,A. This approach is the above-mentioned metallic element 10 - 1500 mg/m2 A plating layer front face is equipped with the coat which consists of oxides which contain oxygen 0.5 to 30%. However, in the steel plate currently indicated here, the improvement effect of a moldability is not enough.
[0006]

[Problem(s) to be Solved by the Invention] It is effective to perform metal plating thick on the front face of a plating layer for improving the moldability of an alloying hot-dip zinc-coated carbon steel sheet just like a cold rolled steel plate. According to research of this invention persons, the coating weight of a metal plating coat is 2000 mg/m2. If it is above, a moldability can be raised to the level almost near a cold rolled steel plate. The coating weight of a metal plating coat is 2000 mg/m2. If it decreases, a moldability improvement effect will decrease, and it is 100 mg/m2. In the following, it became clear that it fell even to the alloying hot-dip zinc-coated carbon steel sheet which effectiveness is lost and is hardly equipped with a metal plating coat, and equivalent level. However, 2000 mg/m2 It is not easy to perform the above thick metal plating often [productivity] and economically.
[0007] The purpose of this invention is to offer the alloying hot-dip zinc-coated carbon steel sheet excellent in the moldability which solves the above-mentioned trouble and can be efficiently manufactured by low cost, and its manufacture approach.
[0008]
[Means for Solving the Problem] this invention persons acquired the following knowledge, as a result of repeating research wholeheartedly about the approach of improving the sliding nature of a plating layer front face, paying attention to sliding nature with the metal mold in the plating layer front face at the time of carrying out press forming having influenced greatly, in order to have improved the moldability of an alloying hot-dip zinc-coated carbon steel sheet just like base material steel plates (for example, a cold rolled steel plate, a hot rolled steel plate, etc.). [finishing / annealing]
[0009] a. Sliding nature is improved because the shape of surface type of alloying hot dip zincing sets the diameter of average crystal grain of the Fe-Zn crystal grain of a plating layer front face to 5 micrometers or less. It is guessed because the lubrication effectiveness to the lubricating oil used at the time of a press is improved according to an operation of a plating layer front face becoming smooth because the crystal grain of a plating layer front face becomes detailed, and contact to the plating layer front face at the time of press working of sheet metal being carried out and metal mold becoming close.
[0010] b. In order to raise the sliding nature of a plating layer, it is good to make the front face into the surface state in which the holdout of a lubricating oil is excellent. In an alloying hot-dip-zincing layer front face, what equips a plating layer front face with a zinc oxide is suitable. It is thought that the zinc oxide has oleophilic and has the operation which holds a lubricating oil to the interface of a steel plate and metal mold at the time of a press. It follows on an alloying hot-dip-zincing layer front face at the heating at high temperature at the time of alloying processing, and, generally coating weight is 20 - 60 mg/m2 as a Zn content. The oxide film exists spontaneously. However, for raising sliding nature, it is insufficient in the above-mentioned coating weight, and a thing equipped with much more zinc oxides is good.
[0011] c. A moldability is spoiled, while the sliding friction between both becoming large and becoming easy to generate the flaking of a plating layer, when a plating layer is elasticity relatively to metal mold.
[0012] What equipped the plating layer front face with the hard metal in addition to the above-mentioned zinc oxide has the still better sliding nature of a plating layer. The coating weight of this metal is comparatively little, and is good, and its thing in the condition that the metal and the zinc oxide lived together on the maximum front face (mixture) is good. As a metal, one sort in the ease of an activity to Fe, Co, and nickel or two sorts or more are suitable.
[0013] d. When a plating layer is processed by approaches, such as electroplating by the solution containing a metal ion, and the permutation galvanizing method, a metallic element has the inclination for electrical conductivity to be small, not to deposit on the oxide film which the metal ion dissolution cannot carry out easily, but to deposit into the defective parts (the pinhole produced in an oxide film, thin part of an oxide film, etc.) of a zinc-oxide coat. For this reason, if it processes by the above-mentioned approach, the coat with which the metal and the zinc oxide coexisted (mixture) can be made to have. The plating steel plate which combines moderate sliding nature and press-forming nature by this can be obtained.
[0014] It is completed based on these newly acquired knowledge, and this invention has the summary in the alloying hot-dip zinc-coated carbon steel sheet of a publication, or its manufacture approach given in

(2) following (1).
[0015] (1) the alloying hot-dip-zincing layer top whose surface diameter of average crystal grain Fe is contained seven to 15% of the weight, and is 5 micrometers or less -- the amount of Zn -- 100 - 1000 mg/m2 it is -- a zinc oxide, one sort in Fe, Co, and nickel, or two sorts or more -- the sum total -- 10 - 1000 mg/m2 Alloying hot-dip zinc-coated carbon steel sheet excellent in the moldability characterized by having the surface coat to contain.
[0016] (2) Galvanize using the melting zinc plating bath whose effective aluminum concentration is 0.080 - 0.20 % of the weight to a base material steel plate. After adjusting plating coating weight, heating at 490 degrees C - 550 degrees C and carrying out alloying processing with the heating rate of 20-70 degrees C/second, maintenance in anodic oxidation and/or oxidizing atmosphere gas -- the amount of Zn -- 100 - 1000 mg/m2 it is -- with the processing to which a plating layer front face is made to be equipped with a zinc oxide The solution containing one sort or two sorts or more of metal ions of Fe, Co, and the nickel is used, and it is this metallic element in total 10 - 1000 mg/m2 The manufacture approach of an alloying hot-dip zinc-coated carbon steel sheet given in the above (1) characterized by performing processing made to adhere.
[0017]
[Embodiment of the Invention] On the occasion of operation of this invention, the reason for having set the range of the gestalt and conditions and it up is explained below.
[0018] Although cold rolled sheet steel is desirable, the hot rolled sheet steel from which the surface oxide film was removed is sufficient as the base material of hot dipping. After a manufacturing facility is generally used and performs cleaning by an alkali solution etc., it carries out reduction annealing, after it carries out hot dipping, performs alloying processing and manufactures an alloying hot-dip zinc-coated carbon steel sheet.
[0019] The chemical composition of a plating layer contains Fe seven to 15% of the weight, and the remainder consists of Zn substantially. If Fe content in a plating layer exceeds 15 % of the weight, since powdering nature will deteriorate remarkably, it is not good. It is 13 or less % of the weight preferably. At less than 7 % of the weight, eta-Zn remains [Fe content] more often on a surface, and subsequent paintwork and weldability are not easy to become poor.
[0020] When the diameter of average crystal grain of the Fe-Zn alloy layer of the surface section of an alloying hot-dip-zincing layer exceeds 5 micrometers, even if the frictional resistance between a plating layer and metal mold makes increase and a plating layer front face equipped with the below-mentioned zinc-oxide coat, the improvement effect over flaking-proof nature is not demonstrated. For this reason, the surface diameter of average crystal grain may be 5 micrometers or less. The diameter of average crystal grain is so desirable that it is small. It is possible to make the diameter of average crystal grain small to about 0.5 micrometers also with the usual means.
[0021] The diameter of average crystal grain of the plating layer surface section in this invention is the average computed having assumed to be a diameter, when a surface Fe-Zn alloy observed and carries out the image processing of the part which is not mechanically crushed by the contact to the roll for conveyance etc. for the scale factor of 1000 times or more with a scanning electron microscope and area converts each diameter of crystal grain as an equivalent circle.
[0022] an above-mentioned alloying hot-dip-zincing layer top -- the amount of Zn -- 100 - 1000 mg/m2 it is -- a zinc oxide, one sort in Fe, Co, and nickel, or two sorts or more -- the sum total -- 10-1000mg/m2 It has the coat to contain.
[0023] Compatibility with a lubricating oil is high to a zinc oxide, increases the oil coating weight per unit area to it, and it has the operation make hard to produce the oil film piece in a sliding surface. The amount of Zn of scaling is 100 mg/m2. When not filling, the above-mentioned operation is inadequate, and the moldability of a plating steel plate is not improved. For this reason, the coating weight of a zinc oxide is 100 mg/m2 in the amount of Zn. It considers as the above. They are 200 mg/m2 preferably. It is above.
[0024] The coating weight of a zinc oxide is 1000 mg/m2 at Zn. If it exceeds, the effectiveness of improving sliding nature will be saturated. Moreover, with an economical means, they are 1000 mg/m2.

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Since it is difficult to make a front face equipped with a lot of oxides which exceed, zinc oxides are 1000 mg/m2 in the amount of Zn. It considers as the following. They are 500 mg/m2 preferably. It is the following.

[0025] The class of a zinc oxide and metal made intermingled is limited to one sort in Fe, Co, and nickel, or two sorts or more because it is easy metals to excel in the effectiveness that these metals improve sliding nature, and to make it adhere on an oxide film. the coating weight of these metals -- 10 (case where they are two or more sorts -- the sum total) mg/m2 When not filling, sliding nature at the time of metallic contact with metal mold arising cannot be improved. They are 200 mg/m2 preferably. It is good to consider as the above.

[0026] The coating weight of these metals is 1000 mg/m2. If it exceeds, a metal covers all zinc oxides, the zinc oxide which lives together on a front face will decrease, oil retentivity will be insufficient, and it will become inadequate improving a moldability. In order to avoid this, metaled coating weight is 1000mg/m2. It considers as the following. They are 700 mg/m2 preferably. It is the following.

[0027] Zn content in a zinc oxide specifies the value which carried out detection measurement as an amount of Zn in a zinc oxide by making into the amount of Zn Zn oxide eluted in the with a pH of ten or more solution in the test sample with the mixed water solution of 3% of the weight or more of an ammonium-dichromate solution, and an aqueous ammonia solution. In the above-mentioned mixed solution, since chromic-acid ion acts as inhibitor to a zinc metal, Zn is not dissolved. Since metallic elements, such as Fe, Co, and nickel, are not dissolved with an alkaline solution, only the zinc oxide which exists in a front face can be dissolved alternatively.

[0028] The gestalt of a zinc oxide is ZnO, a ZnO compound, Zn (OH)2, and Zn (OH)2. Although a compound etc. recognizes variety existence in a front face, it dissolves altogether into the aqueous ammonia solution of an ammonium-dichromate solution. In order to think that each of these oxides and hydroxides have oil retentivity, the amount of Zn contained in the oxide prescribes the amount of zinc oxides.

[0029] The steel plate of this invention can be efficiently manufactured by the approach described below. After carrying out alkaline degreasing of the base material steel plate, reduction heating heated at 600 degrees C or more in sufficient reducing atmosphere is performed. Since a base material is a non-annealed material of a cold rolling as, when you need annealing, it heats more than recrystallizing temperature and gives reduction annealing.

[0030] The dew-point of the ambient atmosphere at the time of reduction heating (or reduction annealing) is good to make it the range of -60--20 degree C. Furthermore, when it is the ambient atmosphere whose hydrogen concentration is six to 12 volume % and whose remainder is nitrogen, it is desirable to hold a dew-point in the range of -40--20 degree C. After reduction heating (or reduction annealing), it cools to the temperature near the plating bath temperature, and alloying processing is carried out, after being immersed in a plating bath, pulling up and adjusting coating weight by approaches, such as gas wiping.

[0031] aluminum contained in a hot-dipping bath has the operation which controls the alloying by the interface at the time of hot dipping. As for aluminum content of a plating bath, it is desirable as effective aluminum (all aluminum weight %-totals Fe % of the weight) to consider as 0.080 % of the weight or more.

[0032] Since zeta phase (FeZn13) which is an alloy phase generated in early stages of an alloying reaction is stable, zeta phase formed in early stages grows big and rough and the gestalt remains on a front face in not filling effective aluminum to 0.080% of the weight, it is difficult to make small the diameter of average crystal grain of a surface Fe-Zn alloy. The effective aluminum concentration of a plating bath is good to make 0.20 % of the weight into an upper limit. When aluminum concentration is raised exceeding 0.20 % of the weight, alloying is delayed and there is a possibility that productivity may fall.

[0033] By controlling the conditions which carry out alloying processing, the diameter of average crystal grain of a surface Fe-Zn alloy is set to 5 micrometers or less. After it adjusts plating coating weight, this carries out rapid heating of 490 degrees C - the 550 degrees C of the steel plates which

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became mist and low temperature from plating bath temperature to a 500 degrees C - 530 degrees C alloying processing temperature field more preferably, adjusts the holding time and carries out Fe content of a coat to 7 - 15% of the weight. 20 degrees C /or more of heating rates to alloying processing temperature are [second] 30 degrees C/second or more more preferably, and they are good to carry out in the range 70 degrees C [/second] or less.

[0034] However, the approach of making small the diameter of average crystal grain of the Fe-Zn alloy of a plating layer front face does not need to be limited to an above-mentioned approach. It is related with raising the nucleus occurrence frequency of the Fe-Zn alloy at the time of alloying. By oxidizing the base material front face before plating, or pretreating (reduced iron is generated at the time of reduction annealing, and reactivity becomes high), Fe system plating, nickel system plating, etc. to a base material, and activating a front face from the early stages of a Fe-Zn alloying reaction It is possible to carry out grain refining of the surface Fe-Zn alloy, without changing the heat pattern of alloying.

[0035] The approach of making a zinc oxide and one or more sorts of metals of Fe, Co, and the nickel living together on a plating layer front face The approach to which the above-mentioned metal is made to adhere after performing oxidation treatment to the plating layer front face after alloying processing and making the zinc oxide of the specified quantity adhere to it, After making the above-mentioned metal of the specified quantity adhere to the plating layer after alloying processing, which approach may be used although there is the approach of oxidizing further the zinc or the zinc oxide which exists in a front face, and making the amount of zinc oxides the predetermined range.

[0036] In the front face of the plating layer which alloying ended, the zinc-oxide coat has arisen spontaneously. As a zinc-oxide art for increasing the amount of zinc oxides further and making it the predetermined range, the approach of anodizing a steel plate in the solution of pH 4-10 is easy, and suitable. The processing which holds a steel plate in the 100-350-degree C oxidizing gas which consists a steam of mixed gas, such as saturation content **** nitrogen gas and oxygen gas, is sufficient.

[0037] To the steel plate after alloying processing or zinc-oxide processing, it is one sort in Fe, Co, and nickel, or two sorts or more in total 10 - 1000 mg/m2 It is made to adhere. The approach which is immersed about 2 to 30 seconds as the adhesion approach of these metals into the liquid which dissolved Fe ion, nickel ion, Co ion, etc. into the with a pH of about two to four acidic solution, and carries out permutation plating is advantageous in cost.

[0038] However, the adhesion approach of a metallic element does not need to be limited to the permutation galvanizing method, and can use the approaches of arbitration, such as the electroplating approach of carrying out electrolysis processing in processing liquid, such as an acidic solution containing the with pH2-a pH of about four above-mentioned metal ion, and carrying out electrocrystallization of the above-mentioned metallic element to the part to which the zinc oxide has not adhered, a part with little coating weight, etc. For controlling coating weight, the electroplating approach which energizes quantity of electricity of the specified quantity is desirable.

[0039] In this invention, since a metallic element deposits into the pinhole produced in the zinc-oxide coat, and a part with a thin zinc-oxide coat, the surface coat with which a metallic film and a zinc-oxide coat intermingle and coexist is obtained. The coexistence condition is possible by adjusting coat generating conditions.

[0040] By the approach of this invention, as mentioned above, the metal of the specified quantity is made to adhere to the plating layer front face which carried out alloying processing, and zinc-oxide covering processing may be carried out anew after that. The oxide film art in this case is good by the same approach as above-mentioned one. Thereby, zinc can oxidize alternatively and metals, such as Fe, nickel, and Co, can make the amount of zinc oxides the predetermined range without oxidizing.

[0041] The alloying hot-dip zinc-coated carbon steel sheet used as the base material of the steel plate of this invention can be easily manufactured by using a well-known general alloying hot-dip-zinc-coated-carbon-steel-sheet manufacturing facility. It is still easier if the facility equipped with the alloying furnace of an induction-heating method is used.

[0042]

[Example] To a cold rolled steel plate made from the super-low carbon steel whose thickness is 0.75mm,

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coating weight is 30 - 70 g/m2 by the hot-dipping simulator. Hot dip zincing was given. The effective aluminum concentration of a plating bath was 0.12 % of the weight. With the induction-heating method, the heating rate was changed to 10-100 degrees C/second, this galvanized steel sheet was heated at 480 degrees C - 550 degrees C, the holding time was set as for 5 - 40 seconds, and Fe content of a plating layer obtained [the diameter of average crystal grain of a surface Fe-Zn alloy] the alloying hot-dip zinc-coated carbon steel sheet which is 1-10 micrometers seven to 15% of the weight. While the steel plate temperature of the cooling process after alloying processing was 100-350 degrees C, oxidation treatment in the inside of the atmospheric air which saturated the steam was performed, and the coating weight of a zinc oxide was adjusted to various values. The diameter of average crystal grain of the obtained steel plate observed the 20 or more measurement parts plating layer front face, and asked for it as the average of the diameter into which the image processing of the photograph was taken and carried out by one 2000 times the scale factor of this, and area converted each diameter of crystal grain as an equivalent circle.

[0043] They are current density 1 - 10 A/dm2 in the sulfuric-acid bath pH2-pH4, and whose temperature a plating bath presentation contains one or more 10-100g [/] sorts in Fe ion, nickel ion, and Co ion l. on these steel plate front faces, and are 50 degrees C. It electroplates on conditions and coating weight is per [100] one side - 2000 mg/m2. One or more sorts of metals of Fe, nickel, and Co were made to adhere.

[0044] Permutation plating in which the alloying hot-dip-zinc-coated-carbon-steel-sheet sample which has the same chemical composition as the above and a plating layer is made immersed for 1 - 30 seconds during the permutation plating bath which dissolved the sulfate of nickel, Fe, and Co into the sulfuric-acid solution is performed, and it is a metallic element 1000 mg/m2 It was made to adhere in the following range.

[0045] The coating weight of these metals was measured by the following approaches. It dissolved with the plating layer in the hydrochloric-acid acidic solution, nickel and Co were measured by solution analysis, and Fe was measured with the weight method which measures weight change of a steel plate before and after performing adhesion processing.

[0046] In the ammonium-dichromate content aqueous ammonia solution, the amount of Zn of the zinc oxide exposed to a steel plate front face, without being covered by the metal dissolved the zinc oxide, and detected it as Zn.

[0047] The following approaches estimated the sliding nature of the obtained steel plate. Drawing 1 is the perspective view showing the concept of sliding nature evaluation equipment of evaluating coefficient of friction of a steel plate from the shaping force at the time of carrying out bending shaping of the steel plate in a ditch type. Coefficient of friction measured with this equipment estimated the sliding nature of a steel plate. The test piece 1 is pushed against the dice side 2 in response to the force from the blank holder bead 4. The configuration of the push metallic ornaments 5 is a rectangular parallelepiped-like. It is drawn in the dice slot 3 which is groove parallel opening, a test piece 1 sliding between the dice side 2 and the blank holder bead 4 with descent of the push metallic ornaments 5. Since the insertion pressure of the push metallic ornaments 5 changes according to the sliding nature of a test piece, coefficient of friction of the piece of a related blank test of insertion pressure and a blank holder load can be measured.

[0048] The dimension of a test piece 1 was made into width of face of 30mm, and die length of 270mm, and the cross-section dimension of a bead was made into the hemicycle with a radius of 5mm. What was ground with the abrasive paper of 600# is used for the front face of the dice side 2, the blank holder bead 4, and the push metallic ornaments 5, and it is slushing oil as lubricant in both sides of a test piece 1 Per one side and 2.5 g/m2 It applied and the press fit rate of the push metallic ornaments 3 was considered as a part for 60mm/. The blank holder load was made into four conditions of 750, 1000, 1250, and 1500kgf, calculated the maximum of the insertion pressure of the push metallic ornaments 5 in each case, from the increment (dP) of a blank holder load, and the increment (dF) of the maximum load of push metallic-ornaments insertion pressure, calculated coefficient of friction (mu) by mu=dF / formula which becomes 2 dP, asked for it, and evaluated sliding nature by the following criteria according to the

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value of mu.
[0049] O : mu is or less 0.24 (very good), less than [O:0.24 super-0.28] O (good), less than [**:0.28 super-0.32] ** (defect), and x:0.32 ** (very defect).
The following approaches estimated the moldability of the obtained steel plate. The cupping draw trial which fabricates a test piece with 0.75mm [in thickness] and a diameter [phi] of 60mm in a cylinder using punch with an outer diameter of 34mm and 35.5mm dice of apertures was performed, the blank holder force (BHF) was changed, and the crack generating boundary was investigated. Tool polish: It is the slushing oil of 60mm a part for /and marketing in polish and shaping rate at abrasive paper #600 0.5 g/m2 The value of BHF just before a crack occurs in the condition of having applied estimated.
[0050] the alloying hot dip zincing which the blank holder force at the time of performing the same cupping draw trial as the above in the cold rolled steel plate [finishing / annealing] which has the same chemical composition as the above-mentioned alloying hot-dip zinc-coated carbon steel sheet is 3500Kgf(s), and does not perform zinc-oxide metallurgy group adhesion processing -- in the steel plate as it is, 2000Kgf was a boundary. For this reason, the following criteria estimated the moldability of the obtained plating steel plate.
[0051] What [... Defect (x).] crack generating does not produce in 3000Kgf(s) ... They are fitness (O) and 2500 or more Kgves [less than 3000] very much... Fitness (O), 2000 or more Kgves [less than 3000] ... They are a defect (**) and less than 2000 Kgves a little. Various kinds of test results were shown in Table 1.
[0052]
[Table 1]

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試験番号	めっき層表面の平均結晶粒径 (μm)	めっき付着量 (g/m²)	めっき層中の鉄含有量 (重量%)	金属付着量 (mg/m²) Fe	Ni	Co	酸化亜鉛中のZn量 mg/m²	摺動性	プレス成形性	備考
1	5	60	7	20	0	0	800	○	○	本発明例
2	3	45	9	350	0	0	450	◎	◎	
3	2	60	10	700	0	0	250	◎	◎	
4	1	45	11	0	10	0	1000	○	○	
5	2	55	9	0	450	0	300	◎	◎	
6	2	45	12	0	950	0	150	○	○	
7	3	55	9	0	0	30	850	○	○	
8	1	40	13	0	0	100	900	○	○	
9	2	35	15	0	0	350	450	◎	◎	
10	2	55	11	30	30	0	750	○	○	
11	2	50	9	100	100	0	250	◎	◎	
12	2	55	11	100	0	180	500	◎	◎	
13	2	70	9	0	250	150	350	◎	◎	
14	5	40	10	100	450	200	120	○	○	
15	1	55	8	100	600	300	100	○	○	
21	* 6	40	10	0	100	0	400	△	△	比較例
22	* 10	40	9	0	200	0	500	△	△	
23	4	45	12	0	0	*<10	* 60	×	×	
24	3	50	10	0	*<10	0	120	△	×	
25	2	45	11	500	0	0	* 60	△	△	
26	2	55	10	0	800	0	* 80	△	△	
27	1	40	10	1000	0	0	* 50	○	△	
28	2	60	11	0	*<10	0	200	△	×	
29	2	50	10	0	*<10	0	850	△	△	
30	2	45	9	0	*<10	0	1000	△	△	
31	2	40	8	100	600	0	* 80	○	△	
32	2	50	11	300	600	0	* 50	△	△	
33	2	55	13	100	700	0	* 80	△	△	
34	3	30	10	60	20	0	* 80	×	×	

注. *印は本発明が規定する範囲外であることを表す。

[0053] As shown in Table 1, the test numbers 1-15 which fulfill the conditions which this invention specifies all showed good sliding nature and a good moldability. the zinc-oxide coating weight which is the range desirable especially -- 200 - 1000 mg/m2 and metal coating weight -- 200 - 700 mg/m2 it was -- test numbers 2, 3, 5, and 9, and 11-13 were very good.

[0054] On the other hand, the test numbers 21 and 22 which this invention specifies [the diameter of average crystal grain of a plating layer front face] and which were out of range, and metal coating weight are 10 mg/m2. The property that the test number 24 which was not filled, 28-30, etc. can creep was not desirable. The test numbers 25-27 with which the amount of zinc in a zinc oxide did not fill the range which this invention specifies, and 31-34 did not have a good moldability. Especially the test number 23 that had both few metal coating weight and amounts of Zn especially than the minimum which this invention specifies was not good.

[0055]

[Effect of the Invention] Since a sliding friction with metal mold has the surface coat which was excellent in the holdout of a lubricating oil few on a smooth plating layer front face, the alloying hot-dip

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zinc-coated carbon steel sheet of this invention has the outstanding sliding nature and the outstanding moldability. Moreover, the steel plate of this invention can be efficiently manufactured by low cost. Therefore, the steel plate of this invention is very suitable for the application of the steel plate for automobile car bodies etc.

[Translation done.]

h g cg b eb cg e e

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最終頁に続く

(54)【発明の名称】　成形性に優れた合金化溶融亜鉛めっき鋼板およびその製造方法

(57)【要約】
【課題】　低コストで効率的に製造できる、成形性に優れた合金化溶融亜鉛めっき鋼板およびその製造方法を提供する。
【解決手段】　Ｆｅ：７～１５重量％含有し、表面の平均結晶粒径が５μｍ以下である合金化溶融亜鉛めっき層の上に、Ｚｎ量が１００～１０００ｍｇ／ｍ^2 である酸化亜鉛と、Ｆｅ、Ｃｏ、Ｎｉの内の１種または２種以上を合計で１０～１０００ｍｇ／ｍ^2 とを含有する表面皮膜を有する合金化溶融亜鉛めっき鋼板。この鋼板は、有効Ａｌ濃度が０．０８０～０．２０重量％の溶融亜鉛めっき浴を用いてめっきし、めっき付着量調整後、２０～７０℃／秒の加熱速度で４９０℃～５５０℃に加熱して合金化処理し、その上にＦｅ、Ｃｏ、Ｎｉの内の１種以上と酸化亜鉛とを含有する表面皮膜を備えさせることで製造できる。

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【特許請求の範囲】

【請求項1】　Feを7～15重量%含有し、表面の平均結晶粒径が5μm以下である合金化溶融亜鉛めっき層の上に、Zn量が100～1000mg/m² である酸化亜鉛と、Fe、Co、Niの内の1種または2種以上を合計で10～1000mg/m² とを含有する表面皮膜を有することを特徴とする成形性に優れた合金化溶融亜鉛めっき鋼板。

【請求項2】　母材鋼板に有効Al濃度が0.080～0.20重量%である溶融亜鉛めっき浴を用いてめっきし、めっき付着量を調整し、20～70℃/秒の加熱速度で490℃～550℃に加熱して合金化処理した後、陽極酸化および/または酸化性雰囲気ガス中での保持によりZn量が100～1000mg/m² である酸化亜鉛をめっき層表面に備えさせる処理と、Fe、Co、Niの内の1種または2種以上の金属イオンを含有する溶液を用いて該金属元素を合計で10～1000mg/m² 付着させる処理とを施すことを特徴とする請求項1に記載の成形性に優れた合金化溶融亜鉛めっき鋼板の製造方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、自動車車体部品等のプレス加工が施される用途に好適な、加工時の耐めっき剥離性の良好な合金化溶融亜鉛めっき鋼板およびその製造方法に関する。

【0002】

【従来の技術】近年、家電、建材、及び自動車の産業分野においては溶融亜鉛めっき鋼板が大量に使用されているが、とりわけ経済性、防錆機能、塗装後の性能が優れている合金化溶融亜鉛めっき鋼板が広く用いられている。合金化溶融亜鉛めっき鋼板は、溶融亜鉛めっき鋼板を合金化処理温度に加熱し、Znめっき層をFe-Zn合金化して製造される。めっき層はFe-Zn金属間化合物よりなり、その平均のFe含有量は通常8～12重量%である。

【0003】合金化溶融亜鉛めっき鋼板のプレス成形性（以下、単に「成形性」とも記す）は、めっき層を有さない鋼板に比較して劣るとされている。それは表面のめっき層が成形時の鋼板の変形を妨げるのが原因とされている。また、プレス加工時に、パウダリング（めっき層が粉末状に剥離する不良現象）やフレーキング（プレス加工に際してめっき層が薄片状になって剥離する不良現象）が発生するとめっき表面での摺動性が悪くなり鋼板のダイス孔への流入抵抗が増すことも成形性が損なわれる原因となる。

【0004】特開平4-202786号公報および特開平4-202787号公報には、亜鉛系めっき鋼板、特に合金化溶融亜鉛めっき鋼板の上に複数のFe系合金電気めっき層を設け、表面の物性を変化させることによって、成形時に生じ易いめっき層の亀裂発生を防止し、電着塗装性と成形性を向上させる技術が開示されている。しかしながらここに開示されている技術では、溶融めっき層の上に多層の電気めっき層を設ける必要があるために製造コストが高くなり生産性も阻害されるという問題があった。

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【0005】特開平8-158066号公報には、めっき層の上にFe-Ni-O系の酸化物皮膜を表面に有する、プレス成形性、溶接性、接着性および化成処理性に優れた亜鉛系めっき鋼板が開示されている。この方法は上記の金属元素を10～1500mg/m² と酸素を0.5～30%含有する酸化物で構成される皮膜をめっき層表面に備えるものである。しかしながらここに開示されている鋼板においても成形性の改善効果は十分ではない。

【0006】

【発明が解決しようとする課題】合金化溶融亜鉛めっき鋼板の成形性を冷間圧延鋼板並に改善するにはめっき層の表面に厚い金属めっきを施すのが有効である。本発明者らの研究によれば、金属めっき皮膜の付着量が2000mg/m² 以上であれば冷間圧延鋼板にほぼ近いレベルまで成形性を向上させることができる。金属めっき皮膜の付着量が2000mg/m² よりも少なくなると成形性改善効果が少なくなり、100mg/m² 未満では殆ど効果がなくなり、金属めっき皮膜を備えない合金化溶融亜鉛めっき鋼板と同等レベルにまで低下することが判明した。しかしながら2000mg/m² 以上の厚い金属めっきを生産性良くしかも経済的に施すのは容易ではない。

【0007】本発明の目的は、上記の問題点を解決し、低コストで効率的に製造できる、成形性に優れた合金化溶融亜鉛めっき鋼板およびその製造方法を提供することにある。

【0008】

【課題を解決するための手段】本発明者らは、合金化溶融亜鉛めっき鋼板の成形性を母材鋼板（例えば、焼鈍済みの冷間圧延鋼板や熱間圧延鋼板など）並に改善するには、プレス成形する際のめっき層表面での金型との摺動性が大きく影響していることに着目し、めっき層表面の摺動性を改善する方法について鋭意研究を重ねた結果、以下のような知見を得た。

【0009】a．合金化溶融亜鉛めっきの表面形状は、めっき層表面のFe-Zn結晶粒の平均結晶粒径を5μm以下とすることで摺動性が改善される。めっき層表面の結晶粒が微細になることでめっき層表面が滑らかになり、プレス加工される際のめっき層表面と金型との接触が緊密になるなどの作用により、プレス時に使用される潤滑油などによる潤滑効果が改善されるためと推測される。

【0010】b．めっき層の摺動性を向上させるために

はその表面を潤滑油の保持性が優れる表面状態にするのがよい。合金化溶融亜鉛めっき層表面においては、酸化亜鉛をめっき層表面に備えるものが好適である。酸化亜鉛は親油性を有しており、プレス時に鋼板と金型との界面に潤滑油を保持する作用があるものと考えられる。合金化溶融亜鉛めっき層表面には、合金化処理時の高温加熱に伴い、一般的に、付着量がＺｎ含有量として２０～６０ｍｇ／ｍ^2 の酸化皮膜が自然発生的に存在している。しかしながら摺動性を向上させるには上記付着量では不足であり、さらに多くの酸化亜鉛を備えているものがよい。。

【００１１】ｃ．めっき層が金型に対して相対的に軟質である場合には両者間での摺動抵抗が大きくなり、めっき層のフレーキングが発生しやすくなるとともに成形性が損なわれる。

【００１２】前述の酸化亜鉛に加えて、めっき層表面に硬質な金属を備えたものはめっき層の摺動性が更に良好である。この金属の付着量は比較的少量でよく、金属と酸化亜鉛が最表面に共存（混在）した状態のものがよい。金属としては、作業の容易さからＦｅ、Ｃｏ、Ｎｉの内の１種または２種以上が好適である。

【００１３】ｄ．金属イオンを含有した溶液による電気めっき法、置換めっき法などの方法によりめっき層を処理すると、金属元素は、電気伝導度が小さく、また、金属イオン溶解のしにくい酸化皮膜上には析出せず、酸化亜鉛皮膜の欠陥部分（酸化皮膜に生じるピンホールや酸化皮膜の薄い部分等）に析出する傾向を有する。このため、上記の方法により処理すれば、金属と酸化亜鉛が共存（混在）した皮膜を備えさせることができる。これにより、適度の摺動性とプレス成形性とを兼ね備えためっき鋼板を得ることができる。

【００１４】本発明はこれらの新たに得られた知見を基にして完成されたものであり、その要旨は下記の（１）に記載の合金化溶融亜鉛めっき鋼板、または、（２）に記載のその製造方法にある。

【００１５】（１）Ｆｅを７～１５重量％含有し、表面の平均結晶粒径が５μｍ以下である合金化溶融亜鉛めっき層の上に、Ｚｎ量が１００～１０００ｍｇ／ｍ^2 である酸化亜鉛と、Ｆｅ、Ｃｏ、Ｎｉの内の１種または２種以上を合計で１０～１０００ｍｇ／ｍ^2 とを含有する表面皮膜を有することを特徴とする成形性に優れた合金化溶融亜鉛めっき鋼板。

【００１６】（２）母材鋼板に有効Ａｌ濃度が０．０８０～０．２０重量％である溶融亜鉛めっき浴を用いてめっきし、めっき付着量を調整し、２０～７０℃／秒の加熱速度で４９０℃～５５０℃に加熱して合金化処理した後、陽極酸化および／または酸化性雰囲気ガス中での保持によりＺｎ量が１００～１０００ｍｇ／ｍ^2 である酸化亜鉛をめっき層表面に備えさせる処理と、Ｆｅ、Ｃｏ、Ｎｉの内の１種または２種以上の金属イオンを含有する溶液を用いて該金属元素を合計で１０～１０００ｍｇ／ｍ^2 付着させる処理とを施すことを特徴とする上記（１）に記載の合金化溶融亜鉛めっき鋼板の製造方法。

【００１７】

【発明の実施の形態】本発明の実施に際し、その形態や条件の範囲およびそれを設定した理由について以下に述べる。

【００１８】溶融めっきの母材は、冷延鋼板が好ましいが、表面の酸化皮膜を除去した熱延鋼板でも構わない。製造設備は一般に使用されるものであり、アルカリ溶液などによる脱脂を行った後、還元焼鈍し、溶融めっきした後、合金化処理を施して合金化溶融亜鉛めっき鋼板を製造する。

【００１９】めっき層の化学組成は、Ｆｅを７～１５重量％含有し、残部は実質的にＺｎよりなる。めっき層中のＦｅ含有量が１５重量％を超えると、パウダリング性が著しく劣化するので良くない。好ましくは１３重量％以下である。Ｆｅ含有量が７重量％未満では表層にη－Ｚｎが残存することが多くなり、以降の塗装性、溶接性が不良となり良くない。

【００２０】合金化溶融亜鉛めっき層の表層部のＦｅ－Ｚｎ合金層の平均結晶粒径が５μｍを超えるとめっき層と金型との間の摩擦抵抗が増し、めっき層表面に後述の酸化亜鉛皮膜を備えさせても耐フレーキング性に対する改善効果が発揮されない。このため表面の平均結晶粒径は５μｍ以下とする。平均結晶粒径は小さいほど好ましい。通常の手段でも平均結晶粒径を０．５μｍ程度にまで小さくすることは可能である。

【００２１】本発明におけるめっき層表層部の平均結晶粒径は、表層のＦｅ－Ｚｎ合金が搬送用のロールへの接触などにより機械的に押しつぶされていない部分を走査型電子顕微鏡で１０００倍以上の倍率で観察し、画像処理してそれぞれの結晶粒径を面積が等価な円として換算した場合に直径と仮定して算出した平均値である。

【００２２】上述の合金化溶融亜鉛めっき層の上には、Ｚｎ量が１００～１０００ｍｇ／ｍ^2 である酸化亜鉛と、Ｆｅ、Ｃｏ、Ｎｉの内の１種または２種以上を合計で１０～１０００ｍｇ／ｍ^2 とを含有する皮膜を備える。

【００２３】酸化亜鉛には、潤滑油との親和性が高く、単位面積当たりの油付着量を増し摺動面での油膜切れを生じ難くする作用がある。表面酸化のＺｎ量が１００ｍｇ／ｍ^2 に満たない場合には上記の作用が不十分であり、めっき鋼板の成形性が改善されない。このため、酸化亜鉛の付着量はＺｎ量で１００ｍｇ／ｍ^2 以上とする。好ましくは２００ｍｇ／ｍ^2 以上である。

【００２４】酸化亜鉛の付着量がＺｎで１０００ｍｇ／ｍ^2 を超えると摺動性を改善する効果が飽和する。また、経済的な手段では１０００ｍｇ／ｍ^2 を超えるような大量の酸化物を表面に備えさせることは困難であるの

で、酸化亜鉛はZn量で1000mg／m² 以下とする。好ましくは500mg／m² 以下である。

【0025】酸化亜鉛と混在させる金属の種類をFe、Co、Niの内の1種または2種以上に限定するのは、これらの金属が摺動性を改善する効果に優れることと、酸化皮膜上に付着させるのが容易な金属であるからである。これらの金属の付着量が（2種以上である場合にはその合計で）10mg／m² に満たない場合には、金型との金属接触が生じた際の摺動性を改善することができない。好ましくは200mg／m² 以上とするのがよい。

【0026】これらの金属の付着量が1000mg／m² を超えると、金属が酸化亜鉛を覆い尽くし、表面に共存する酸化亜鉛が少なくなり、保油性が不足して成形性の改善が不十分となる。これを避けるために金属の付着量は1000mg／m² 以下とする。好ましくは700mg／m² 以下である。

【0027】酸化亜鉛中のZn含有量は、測定用試料を3重量%以上の重クロム酸アンモニウム溶液とアンモニア水溶液の混合水溶液でpH10以上の溶液中に、溶出したZn酸化物をZn量として検出測定した値を酸化亜鉛中のZn量として規定する。上記混合溶液ではクロム酸イオンが亜鉛金属に対するインヒビターとして作用するのでZnは溶解しない。Fe、Co、Ni等の金属元素はアルカリ性溶液では溶解しないので、表面に存在する酸化亜鉛のみを選択的に溶解させることができる。

【0028】酸化亜鉛の形態はZnO、ZnO化合物、$Zn(OH)_2$、$Zn(OH)_2$ 化合物など表面には多種存在するが、重クロム酸アンモニウム溶液のアンモニア水溶液中にはすべて溶解する。これらの酸化物および水酸化物はいずれも保油性があるものと考えるため、酸化物に含有されているZn量にて、酸化亜鉛量を規定するものである。

【0029】本発明の鋼板は以下に述べる方法で効率的に製造できる。母材鋼板をアルカリ脱脂した後、十分な還元雰囲気中で600℃以上に加熱しする還元加熱を施す。母材が冷間圧延ままの未焼鈍材であるために焼鈍を必要とする場合には再結晶温度以上に加熱して還元焼鈍を施す。

【0030】還元加熱（または還元焼鈍）時の雰囲気の露点は、－60～－20℃の範囲にするのがよい。さらには、水素濃度が6～12体積%、残部が窒素である雰囲気の場合には、露点を－40～－20℃の範囲に保持することが好ましい。還元加熱（または還元焼鈍）後にはめっき浴温度近傍の温度に冷却し、めっき浴に浸漬し、引き上げてガスワイピング等の方法で付着量を調整した後、合金化処理する。

【0031】溶融めっき浴に含有されるAlは、溶融めっき時の界面での合金化を抑制する作用がある。めっき浴のAl含有量は、有効Al（全Al重量%－全Fe重量%）として、0.080重量%以上とするのが好ましい。

【0032】合金化反応の初期に生成する合金相であるζ相（$FeZn_{13}$）が安定であるため、有効Alが0.080重量%に満たない場合には、初期に形成されたζ相が粗大に成長し、その形態が表面に残存するので、表層のFe－Zn合金の平均結晶粒径を小さくすることが困難である。めっき浴の有効Al濃度は0.20重量%を上限とするのがよい。0.20重量%を超えてAl濃度を高めると、合金化が遅延し、生産性が低下するおそれがある。

【0033】合金化処理する条件を制御することにより、表面のFe－Zn合金の平均結晶粒径を5μm以下とする。これは、めっき付着量を調整した後、めっき浴温度よりもやや低温になった鋼板を、490℃～550℃、より好ましくは500℃～530℃の合金化処理温度領域に急速加熱し、保持時間を調整して皮膜のFe含有量を7～15重量%にする。合金化処理温度への加熱速度は20℃／秒以上、より好ましくは30℃／秒以上で、70℃／秒以下の範囲で行うのが良い。

【0034】しかしながら、めっき層表面のFe－Zn合金の平均結晶粒径を小さくする方法は上述の方法に限定される必要はない。合金化時のFe－Zn合金の核発生頻度を高めることに関しては、めっき前の母材表面を酸化させたり（還元焼鈍時に還元鉄が生成され、反応性が高くなる）、Fe系めっきやNi系めっきなどの前処理を母材に施し、Fe－Zn合金化反応の初期から表面を活性化させておくことにより、合金化のヒートパターンを変化させることなく、表層Fe－Zn合金を細粒化させることが可能である。

【0035】めっき層表面に酸化亜鉛とFe、Co、Niの内の1種以上の金属とを共存させる方法は、合金化処理後のめっき層表面に酸化処理を施して所定量の酸化亜鉛を付着させた後に上記金属を付着させる方法と、合金化処理後のめっき層に所定量の上記金属を付着させた後、表面に存在する亜鉛または酸化亜鉛をさらに酸化させて酸化亜鉛量を所定の範囲にする方法があるがいずれの方法でも構わない。

【0036】合金化が終了しためっき層の表面には酸化亜鉛皮膜が自然発生的に生じている。酸化亜鉛量を更に増して所定の範囲にするための酸化亜鉛処理方法としては、鋼板をpH4～10の溶液中で陽極酸化する方法が容易であり好適である。鋼板を、水蒸気を飽和量含む窒素ガス、酸素ガスなどの混合ガスからなる100～350℃の酸化性ガス中で保持する処理などでも良い。

【0037】合金化処理後または酸化亜鉛処理後の鋼板に、Fe、Co、Niの内の1種または2種以上を合計で10～1000mg／m² 付着させる。これらの金属の付着方法としては、pH2～4程度の酸性溶液中にFeイオン、Niイオン、Coイオンなどを溶解した液中

に2～30秒程度浸漬し、置換めっきする方法が、コスト的には有利である。

【0038】しかしながら金属元素の付着方法は置換めっき法に限定される必要はなく、pH2～pH4程度の、上記金属イオンを含有する酸性溶液等の処理液中で電解処理して上記金属元素を酸化亜鉛が付着していない部分や付着量が少ない部分などに電析させる電気めっき方法など、任意の方法を用いることができる。付着量を制御するには所定量の電気量を通電する電気めっき方法が好ましい。

【0039】本発明では、酸化亜鉛皮膜内に生じているピンホールや、酸化亜鉛皮膜が薄い部分に金属元素が析出するので、金属皮膜と酸化亜鉛皮膜が混在して共存する表面皮膜が得られる。共存状態は皮膜発生条件を調整することで可能である。

【0040】本発明の方法では、上述したように、合金化処理しためっき層表面に所定量の金属を付着させ、その後にあらためて酸化亜鉛被覆処理してもよい。この場合の酸化皮膜処理方法は前述のと同様の方法で良い。これにより、Fe、Ni、Co等の金属は酸化されないで亜鉛が選択的に酸化されて酸化亜鉛量を所定の範囲にすることができる。

【0041】本発明の鋼板の母材となる合金化溶融亜鉛めっき鋼板は、公知の一般的な、合金化溶融亜鉛めっき鋼板製造設備を使用することにより容易に製造できる。誘導加熱方式の合金化炉を備えた設備を用いればさらに容易である。

【0042】

【実施例】厚さが0．75mmの極低炭素鋼を素材とする冷間圧延鋼板に、溶融めっきシミュレータにより、付着量が30～70g／m^2 の溶融亜鉛めっきを施した。めっき浴の有効Al濃度は0．12重量%であった。この亜鉛めっき鋼板を誘導加熱方式により、加熱速度を10～100℃／秒まで変化させて480℃～550℃に加熱し、保持時間を5～40秒間とし、めっき層のFe含有量が7～15重量%、表面のFe－Zn合金の平均結晶粒径が1～10μmの合金化溶融亜鉛めっき鋼板を得た。合金化処理後の冷却過程の鋼板温度が100～350℃の間に、水蒸気を飽和させた大気中での酸化処理を施して酸化亜鉛の付着量を種々の値に調整した。得られた鋼板の平均結晶粒径は、測定個所20以上のめっき層表面を観察し、倍率2000倍で写真を撮影し、画像処理してそれぞれの結晶粒径を面積が等価な円として換算した直径の平均値として求めた。

【0043】これらの鋼板表面に、めっき浴組成がFeイオン、Niイオンおよびコバルトイオンの内の1種以上を10～100g／ﾘｯﾄﾙ含有し、pH2～pH4、温度が50℃である硫酸浴中で、電流密度1～10A／dm^2 の条件で電気めっきし、付着量が片面当たり100～2000mg／m^2 のFe、Ni、Coの1種以上の金属を付着させた。

【0044】上記と同一の化学組成およびめっき層を有する合金化溶融亜鉛めっき鋼板試料を、硫酸溶液中にNi、Fe、Coの硫酸塩を溶解した置換めっき浴中に1～30秒間浸漬させる置換めっきを行い、金属元素を1000mg／m^2 以下の範囲で付着させた。

【0045】これらの金属の付着量は以下の方法で測定した。NiおよびCoは塩酸酸性溶液中でめっき層と共に溶解して溶液分析によって測定し、Feは付着処理をおこなう前後での鋼板の重量変化を測定する重量法によって測定した。

【0046】金属に被覆されずに鋼板表面に露出している酸化亜鉛のZn量は、重クロム酸アンモニウム含有アンモニア水溶液中に、酸化亜鉛を溶解し、Znとして検出した。

【0047】得られた鋼板の摺動性を以下の方法で評価した。図1は溝型に鋼板を曲げ成形する際の成形力から鋼板の摩擦係数を評価する摺動性評価装置の概念を示す斜視図である。この装置により測定した摩擦係数により鋼板の摺動性を評価した。試験片1はしわ押さえビード4からの力を受けてダイス面2に押し付けられている。押し金具5の形状は直方体状である。押し金具5の下降に伴って試験片1はダイス面2としわ押さえビード4との間で摺動しつつ平行な溝状の開口部であるダイス溝3に引き込まれる。試験片の摺動性に応じて押し金具5の圧入力が変化するので、圧入力としわ押さえ荷重との関係から試験片の摩擦係数を測定することができる。

【0048】試験片1の寸法は幅30mm、長さ270mmとし、ビードの断面寸法は半径5mmの半円形とした。ダイス面2、しわ押さえビード4および押し金具5の表面は、600#の研磨紙で研磨したものを用い、試験片1の両面には潤滑剤として防錆油を片面あたり、2．5g／m^2 塗布し、押し金具3の圧入速度は60mm／分とした。しわ押さえ荷重は、750、1000、1250、1500kgfの4条件とし、それぞれの場合の押し金具5の圧入力の最大値を求め、しわ押さえ荷重の増分（dP）と押し金具圧入力の最大荷重の増分（dF）とから、摩擦係数（μ）を$\mu = dF / 2dP$なる式により計算して求め、μの値にしたがって摺動性を下記の基準で評価した。

【0049】◎：μが0．24以下（極めて良好）、
○：0．24超0．28以下○（良好）、
△：0．28超0．32以下△（不良）、
×：0．32超（極めて不良）。

得られた鋼板の成形性は以下の方法で評価した。厚さ0．75mm、直径60mmφの試験片を外径34mmのポンチ、孔径35．5mmダイスを用いて円筒に成形するカップ絞り試験を行い、しわ押さえ力（BHF）を変化させ、ワレ発生境界を調査した。工具研磨：研磨紙#600で研磨、成形速度60mm／分、市販の防錆油

を０．５ｇ／ｍ² 塗布した状態で、亀裂が発生する直前のＢＨＦの値にて評価した。

【００５０】上記合金化溶融亜鉛めっき鋼板と同一の化学組成を有する焼鈍済みの冷間圧延鋼板では、上記と同様のカップ絞り試験をおこなった際のしわ押さえ力は３５００Ｋｇｆであり、酸化亜鉛や金属付着処理をおこなわない合金化溶融亜鉛めっきそのままの鋼板では、２０００Ｋｇｆが境界であった。このため得られためっき鋼＊

＊板の成形性は以下の基準で評価した。

【００５１】３０００Ｋｇｆでワレ発生の生じないもの・・・極めて良好（◎）、２５００以上３０００Ｋｇｆ未満・・・良好（○）、２０００以上３０００Ｋｇｆ未満・・・やや不良（△）、２０００Ｋｇｆ未満・・・不良（×）。各種の試験結果を表１に示した。

【００５２】

【表１】

試験番号	めっき層表面の平均結晶粒径（μｍ）	めっき付着量（g/m²）	めっき層中の鉄含有量（重量％）	金属付着量（mg/m²） Fe	Ni	Co	酸化亜鉛中のZn量 mg/m²	摺動性	プレス成形性	備考
1	5	60	7	20	0	0	800	○	○	本発明例
2	3	45	9	350	0	0	450	◎	◎	
3	2	60	10	700	0	0	250	◎	◎	
4	1	45	11	0	10	0	1000	○	○	
5	2	55	9	0	450	0	300	◎	◎	
6	2	45	12	0	950	0	150	○	○	
7	3	55	9	0	0	30	850	○	○	
8	1	40	13	0	0	100	900	○	○	
9	2	35	15	0	0	350	450	◎	◎	
10	2	55	11	30	30	0	750	○	○	
11	2	50	9	100	100	0	250	◎	◎	
12	2	55	11	100	0	180	500	◎	◎	
13	2	70	9	0	250	150	350	◎	◎	
14	5	40	10	100	450	200	120	○	○	
15	1	55	8	100	600	300	100	○	○	
21	＊ 6	40	10	0	100	0	400	△	△	比較例
22	＊ 10	40	9	0	200	0	500	△	△	
23	4	45	12	0	0	＊<10	＊ 60	×	×	
24	3	50	10	0	＊<10	0	120	△	×	
25	2	45	11	500	0	0	＊ 60	△	△	
26	2	55	10	0	800	0	＊ 80	△	△	
27	1	40	10	1000	0	0	＊ 50	○	△	
28	2	60	11	0	＊<10	0	200	△	×	
29	2	50	10	0	＊<10	0	850	△	△	
30	2	45	9	0	＊<10	0	1000	△	△	
31	2	40	8	100	600	0	＊ 80	○	△	
32	2	50	11	300	600	0	＊ 50	△	△	
33	2	55	13	100	700	0	＊ 80	△	△	
34	3	30	10	60	20	0	＊ 80	×	×	

注．＊印は本発明が規定する範囲外であることを表す。

【００５３】表１からわかるように、本発明の規定する条件を満たしている試験番号１～１５は、いずれも良好な摺動性と成形性を示した。中でも好ましい範囲である酸化亜鉛付着量が２００～１０００ｍｇ／ｍ² 、金属付着量が２００～７００ｍｇ／ｍ² であった試験番号２、３、５、９および１１～１３は極めて良好であった。

【００５４】これに対し、めっき層表面の平均結晶粒径が本発明の規定する範囲外であった試験番号２１および※50

※２２、金属付着量が１０ｍｇ／ｍ² に満たなかった試験番号２４および２８～３０などはいずれの特性とも好ましくなかった。酸化亜鉛中の亜鉛量が本発明の規定する範囲に満たなかった試験番号２５～２７および３１～３４は成形性がよくなかった。なかでも、金属付着量とＺｎ量が共に本発明の規定する下限よりも少なかった試験番号２３は、特に良くなかった。

【００５５】

【発明の効果】本発明の合金化溶融亜鉛めっき鋼板は、滑らかなめっき層表面に金型との摺動抵抗が少なく潤滑油の保持性に優れた表面皮膜を有するので、優れた摺動性と成形性を兼ね備えている。また本発明の鋼板は、低コストで効率的に製造できる。従って本発明の鋼板は自動車車体用鋼板などの用途に極めて好適である

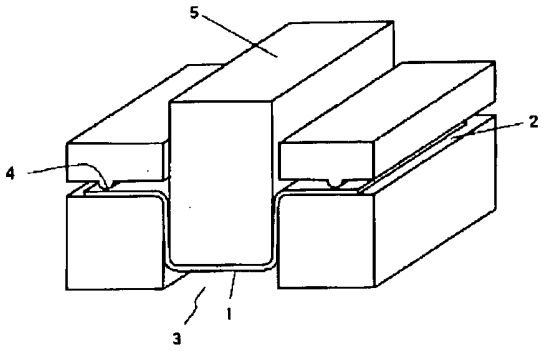
【図面の簡単な説明】

【図１】摺動性評価装置の概念を示す斜視図である。

【符号の説明】

１・・・試験片、２・・・ダイス面、３・・・ダイス溝、４・・・しわ押さえビード、５・・・押し金具。

【図１】



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